Solar-Driven Photocatalytically-Assisted Water Splitting

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PD14

Overview

Timeline

- Start date: Sept. 2007
- End date: Oct. 2011
- Percent complete: 15%

Budget

- Total project funding
  - DOE share: $4M
  - Contractor share: $1M
- $300k received in FY07
- Funding for FY08: $1M

Barriers

- Barriers addressed

U. High-Temperature Thermochemical Technology

V. High-Temperature Robust Materials

W. Concentrated Solar Energy Capital Cost

X. Coupling Concentrated Solar Energy & Thermochemical Cycles

- **H_2 Production Target: $3.00/kg**

Partners

Project lead:

Solar System Development

- FSEC at UCF

Reactor/Receiver & Process Development

Objectives

- Evaluate photo/thermo-chemical water splitting cycles that employ the visible portion of the solar spectrum for production of hydrogen
- Select a cycle that has the best potential for cost-effective production of hydrogen from water – DOE target of **$3.00/kg H_2**
- Demonstrate technical feasibility of the selected cycle using solar input in a bench-scale reactor
- Demonstrate pre-commercial feasibility via a fully-integrated pilot-scale solar hydrogen production system
- Perform economic analysis of the selected cycle.

Project Participants

- Science Applications International Corp.
  - Contract Management
  - Solar Concentration System Development & System Integration
- Florida Solar Energy Center at UCF
  - Photo/Thermo-Chemical Cycle Evaluation/Selection
  - Reactor/Receiver & System Design
- IPHE partnership

Project Phases

- PHASE 1: Sub-cycle testing & evaluation
- PHASE 2: Bench-scale testing of the complete cycle & pilot plant design
- PHASE 3: Pilot-scale demonstration

Milestones, Schedule & Deliverables

Month-Year	Type	Description	Status
Sep '08	Report	Select preferred water-splitting cycle, based on cost & performance evaluations	Complete
Sep '08	Report	Preliminary design of solar concentrator for pilot-scale test system	ongoing
Mar '09	Report	Summary of experimental results & economic analysis, with H_2 cost estimate & recommendations for bench scale system	ongoing
Mar '09	**GO/ NO-GO To Phase 2**	Optimal high temperature water-splitting cycle selected for bench-scale testing & non-federal cost share in place for Phase 2	
Mar '10	Report	Summary of bench-scale reactor & solar system test results	
Mar '10	**GO/ NO-GO To Phase 3**	Bench-scale results prove to be technologically feasible to support scale-up to pilot-scale demonstration & reveal no major technical hurdles Economic analysis shows that the projected cost of hydrogen from this technology will meet 2010 target of **< $3/kg**	
Sep '10	Report	Design of pilot-scale solar concentrator & pilot-scale receiver/reactor	
Apr '11	Report	Completion of concentrator installation; demonstration of dish operation with receiver	
Sep '11	Report	Final report with results of all testing and development, final cost estimates, & recommendations for further development	

Phase 1 Approach

- Sub-cycle Testing & Evaluation
  - Photo/Thermo-Chemical Cycle Analysis
  - Lab Testing of Selected Cycle
  - Report - Preferred Cycle Selection
  - Reactor/Process Configuration
- Solar Concentrator Design
  - Concentrator Specifications
  - Preliminary Concentrator Design
  - Subsystem Tests
  - Report - Prelim. Solar Concentrator Design
- Economic Evaluation

Technical Accomplishments/ Progress/Results

- Completed cycle analyses
- Selected cycle for further development
- Validated hydrogen production photo-process
- Validated oxygen production sub-cycle chemistry
- Evaluated reactor/receiver options
- Evaluated solar collector configurations

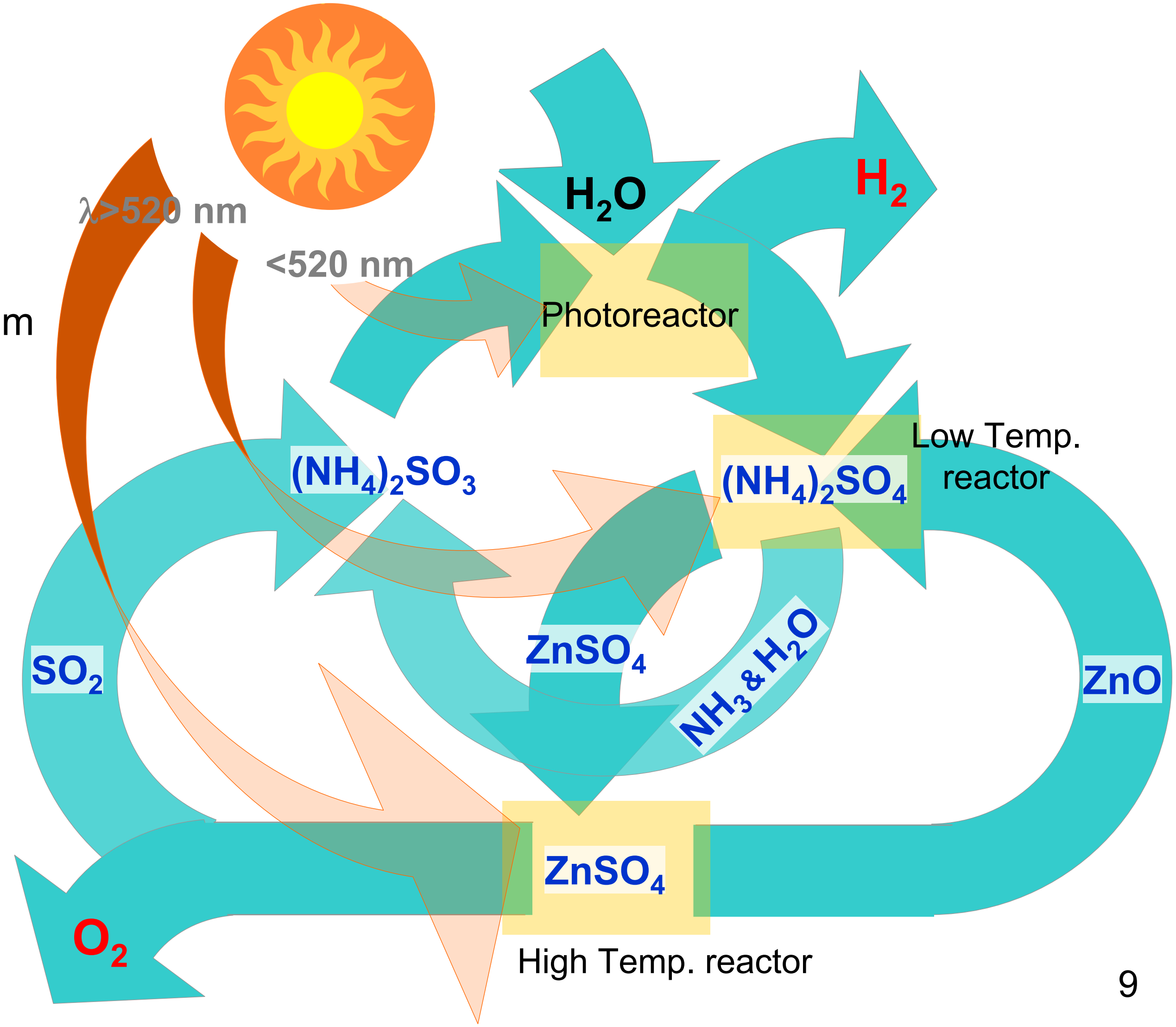
S-NH_3 Solar Water Splitting Cycle

H_2 Production Step

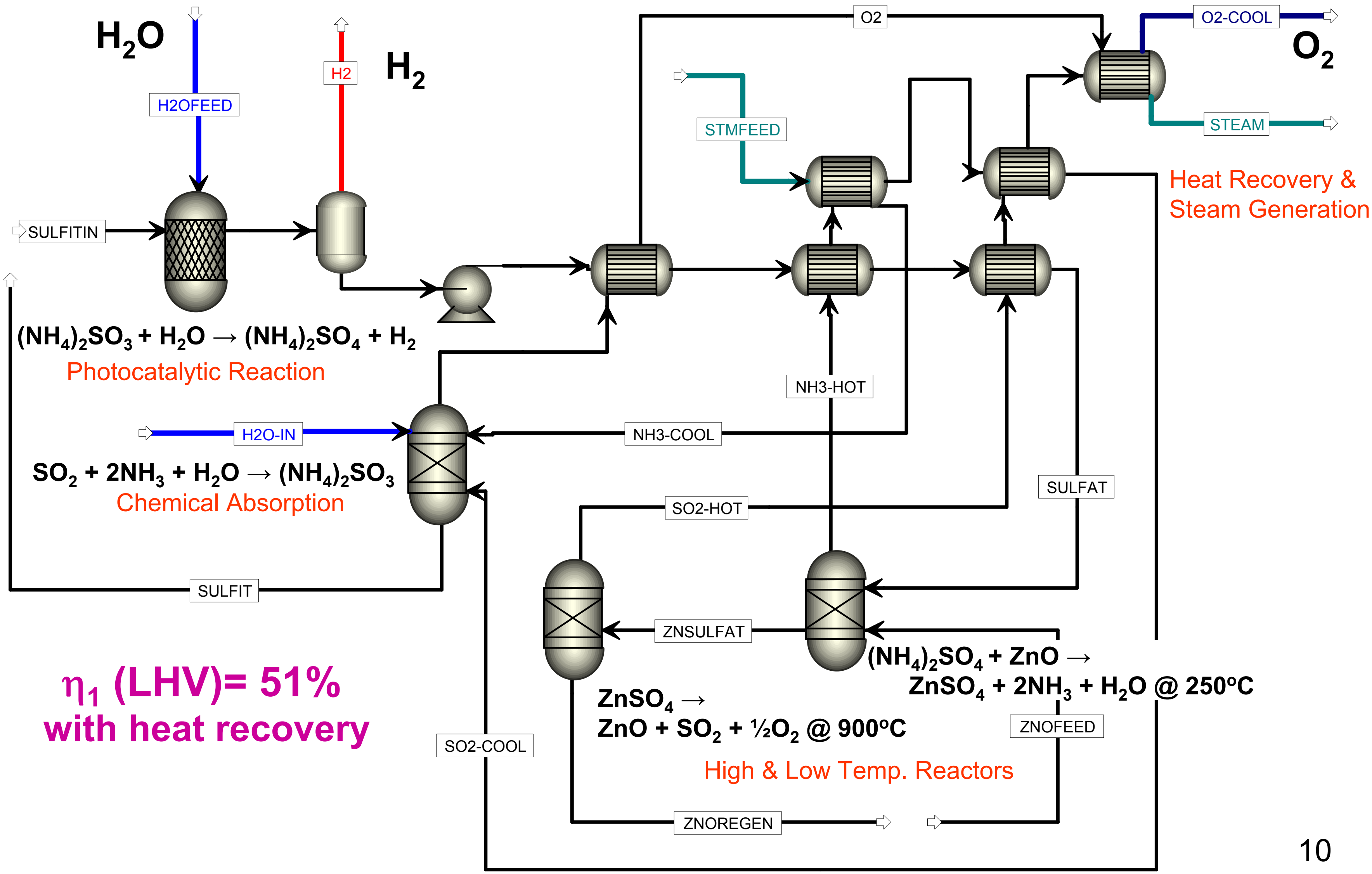
- Photocatalytic
- Operates at λ<520 nm
- Requires ~20% of solar spectrum

O_2 Production Process

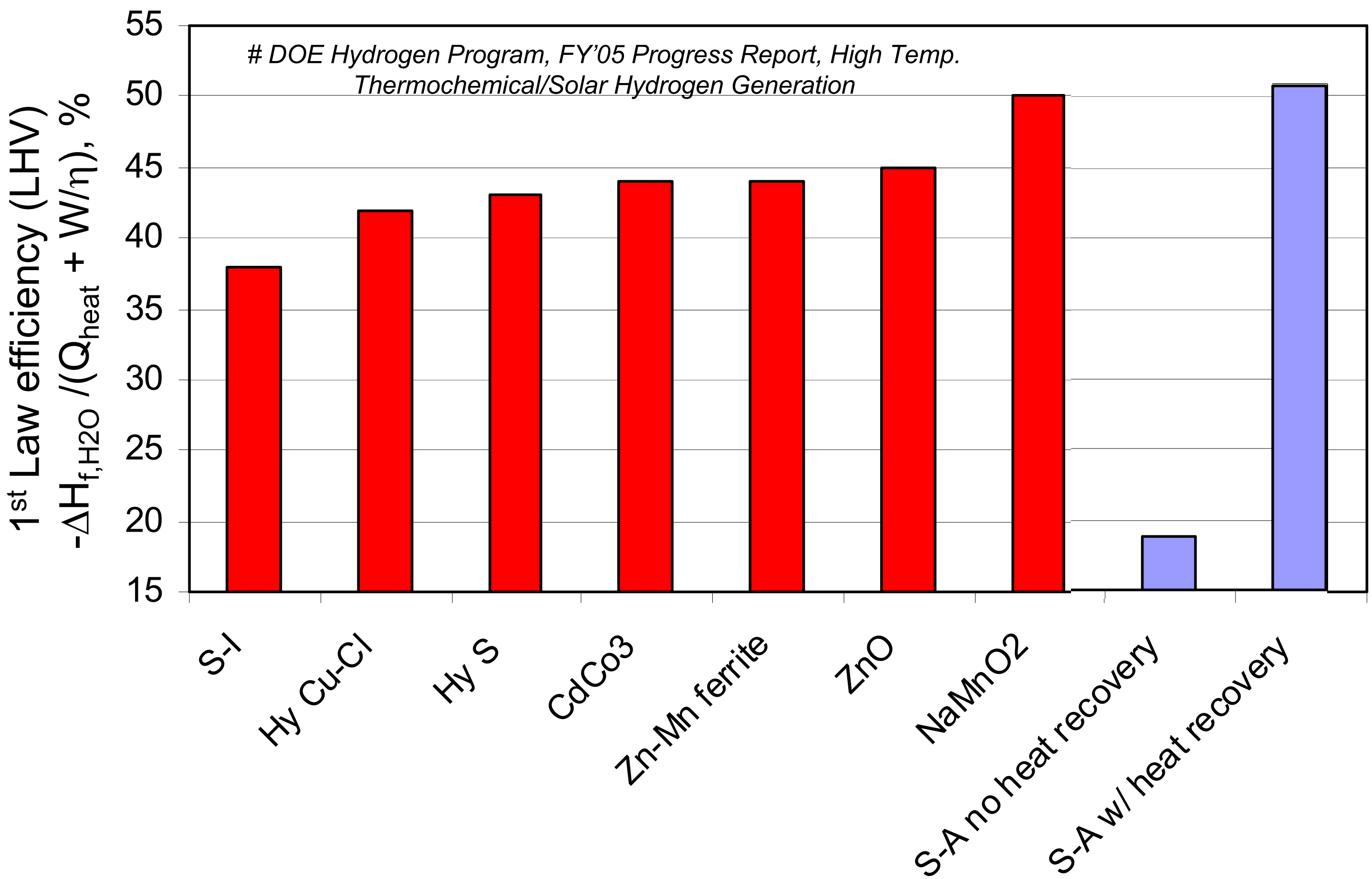
- Thermocatalytic
- Operates at λ>520 nm
- Requires ~80% of solar spectrum



Aspen Flowsheet of S-NH_3 Cycle



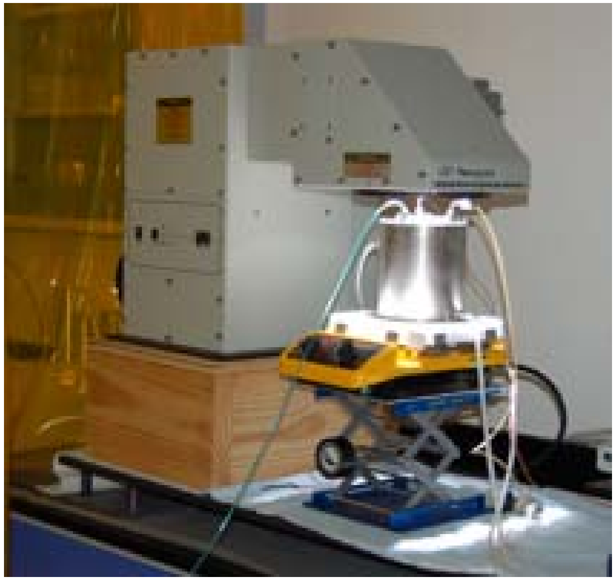
Comparison of S-NH_3 Cycle Efficiency to Other HT Cycles#

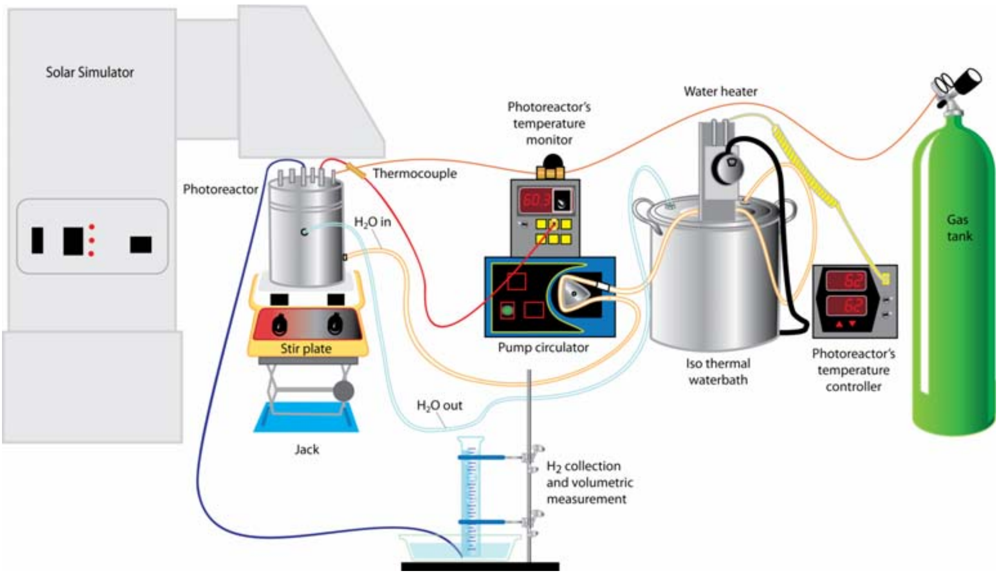


Photocatalyst Screening for Hydrogen Production

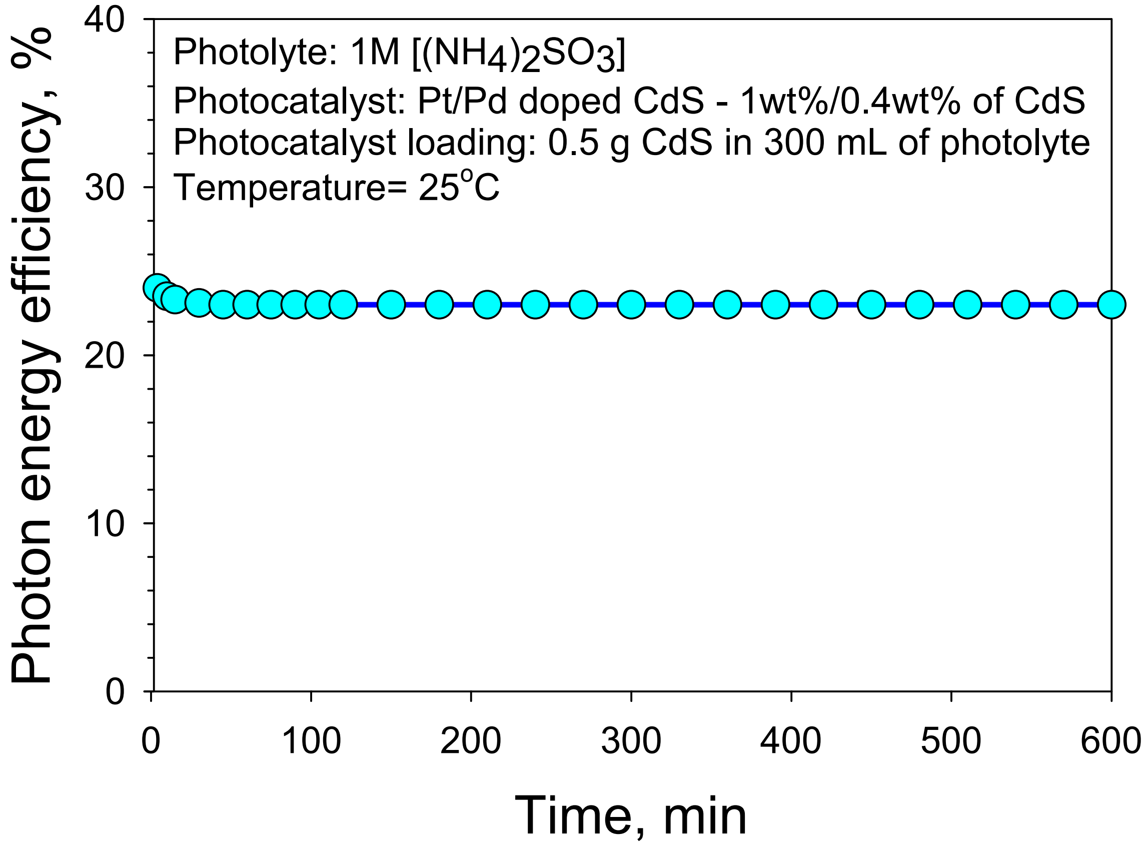
$(NH_4)_2SO_{3(aq)} + H_2O_{(l)} \rightarrow (NH_4)_2\ SO_{4(aq)} + H_{2(g)}$

Setup for Photocatalytic H_2 Production Experiments

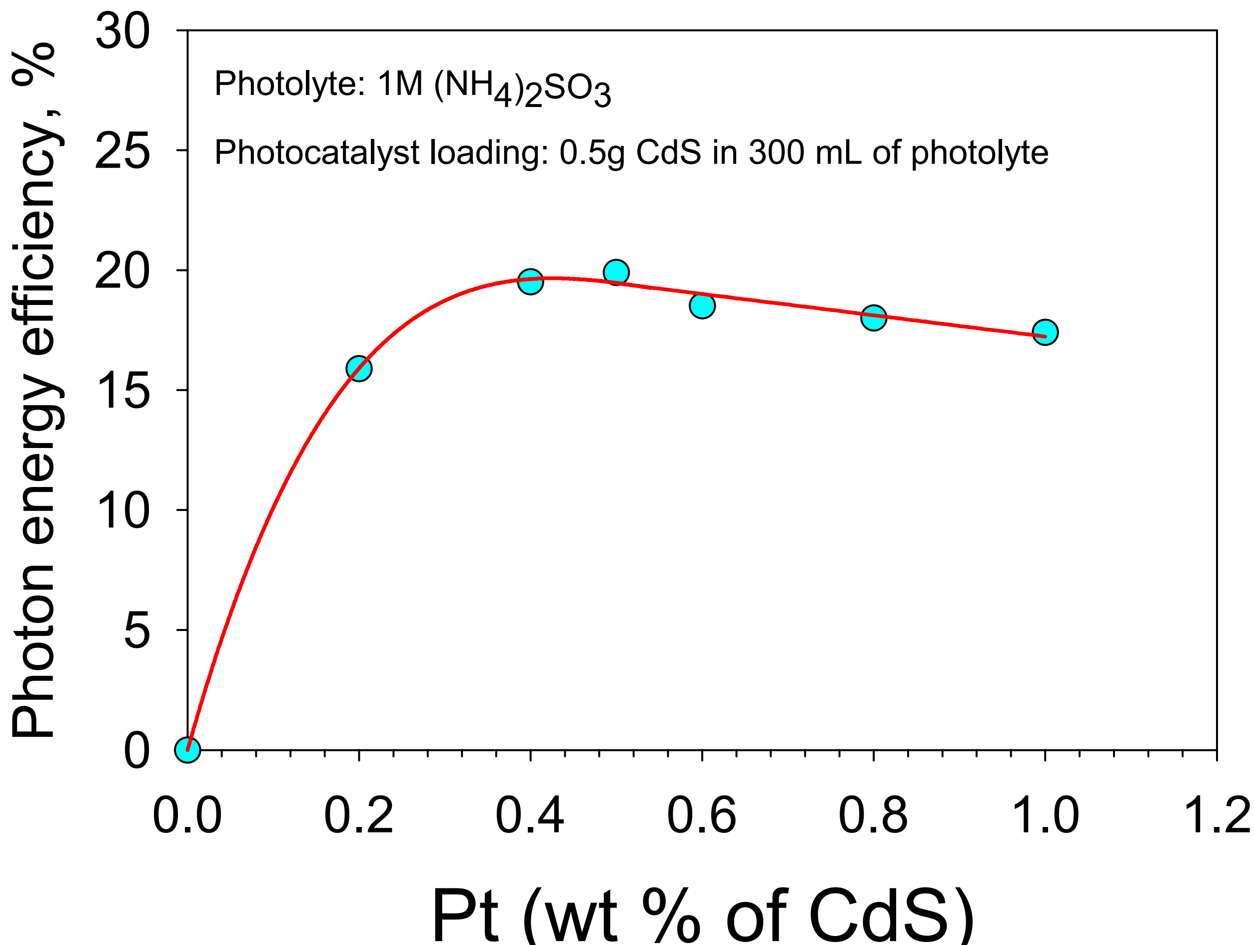




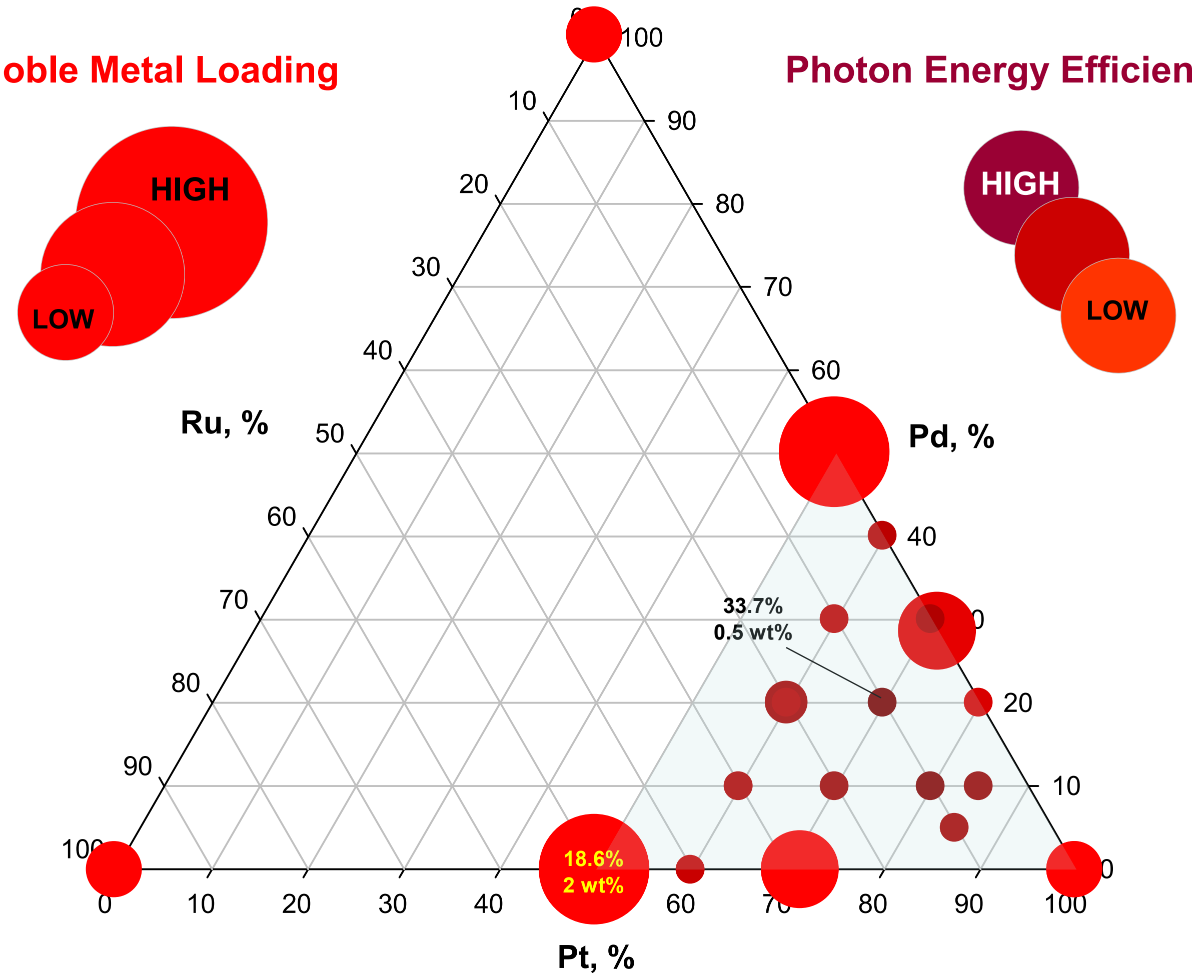
Stability of the Photosystem in Hydrogen Generation Step



Photon Efficiency as a Function of Single Metal Dopant Loading

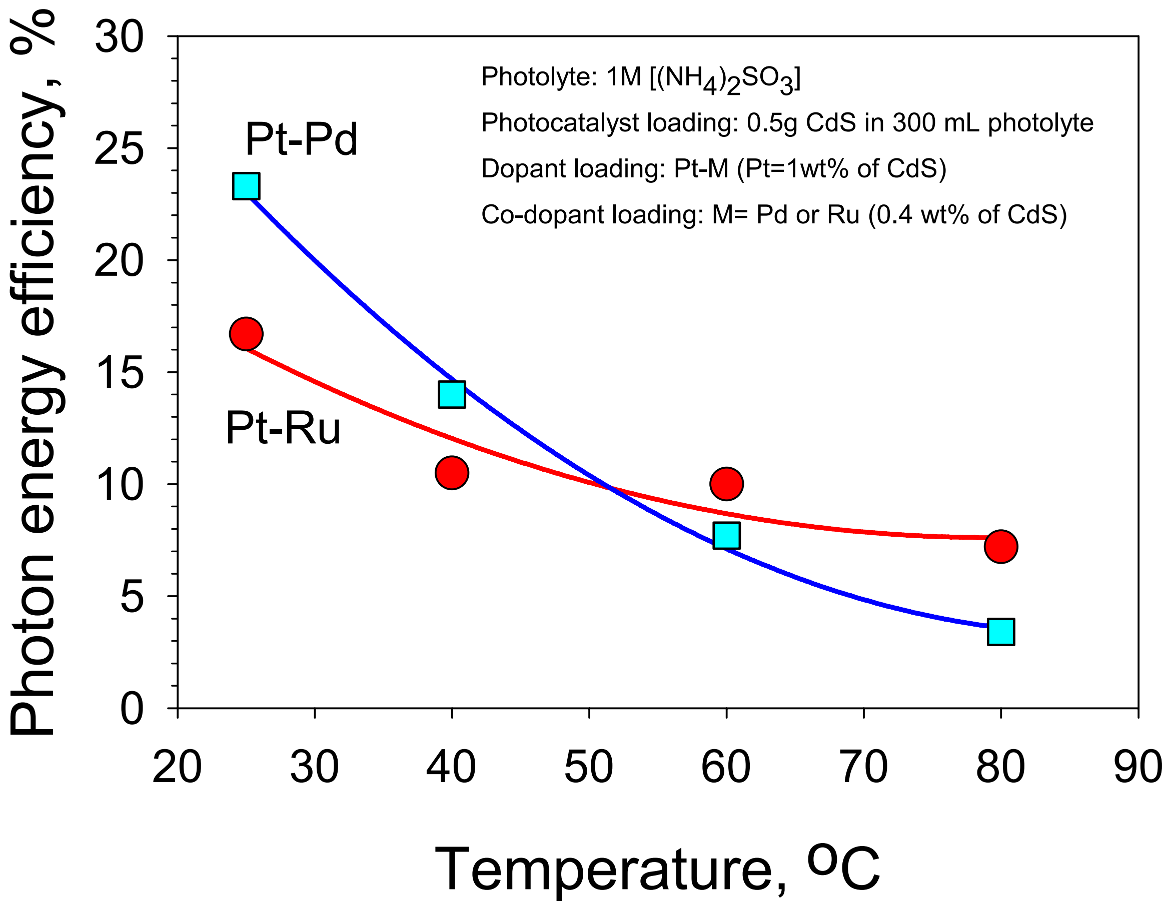


Effect of Photocatalyst Doping



Photocatalyst loading: 0.5 g CdS in 300 mL photolyte: 1M $(NH_4)_2SO_3$

Effect of Photolyte Temperature



Sub-Cycle for Oxygen Production

$$(NH_4)_2SO_{4(s)} + ZnO_{(s)} \rightarrow 2NH_{3(g)} + ZnSO_{4(s)} + H_2O_{(g)}$$

$$ZnSO_{4(s)} \rightarrow SO_{2(g)} + ZnO_{(s)} + \tfrac{1}{2}O_{2(g)}$$

Experimental Methodology

Investigated thermocatalytic decomposition of:

- Pure $(NH_4)_2SO_4$
- $ZnO:(NH_4)_2SO_4$ = 1.5:1 (molar ratio)
- $ZnSO_4$

In the temperature range of 100°C-900°C.

Employing following analytical techniques:

- TG-DTA
- TPD-MS
- GC-MS/UV-Vis

Thermocatalytic Decomposition of $(NH_4)_2SO_4$/ZnO – Summary of Reaction Product Analysis

Method \ T/ °C	100	200	300	400	500	600	700	800
TGA-MS				NH_3 H_2O		SO_3		
GC-MS/UV-Vis						NH_3 H_2O		SO_3 SO_2
TPD-MS				NH_3 H_2O				O_2 SO_2 SO_3

$ZnO/(NH_4)_2SO_4$ Thermocatalytic Decomposition – Reaction Mechanisms

Step 1 (T< ~400°C):

$$(NH_4)_2SO_{4(s)} \rightarrow NH_{3(g)} + NH_4HSO_{4(s)}$$

$$NH_4HSO_{4(s)} + ZnO_{(s)} \rightarrow NH_{3(g)} + H_2O_{(g)} + ZnSO_{4(s)}$$

Step 2 (T<~800°C):

$$ZnSO_{4(s)} \rightarrow ZnO_{(s)} + SO_{3(g)}$$

Step 3 (T>~800°C):

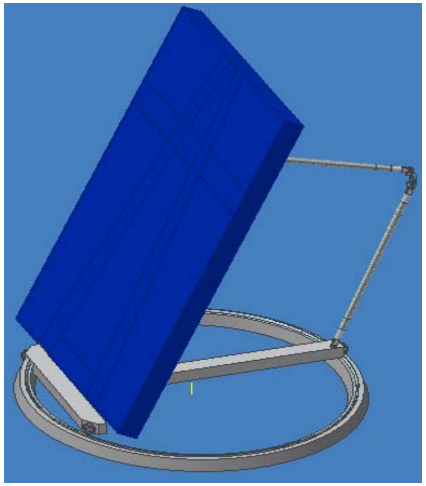
$$ZnSO_{4(s)} \rightarrow ZnO_{(s)} + SO_{2(g)} + \tfrac{1}{2}O_{2(g)}$$

Solar Hydrogen Production
Heliostat Cost Reduction

Heliostats are the largest single cost component in the solar hydrogen production system

Identified potential for cost savings using a GRC (Glass-Reinforced Concrete) heliostat structure :

- Very low cost material ($0.15/kg)
- Easy to process (automated spray on mold)
- Excellent weathering and stiffness
- Excellent design flexibility (molded-in reinforcing ribs and mounts; pre-tensioning is possible)



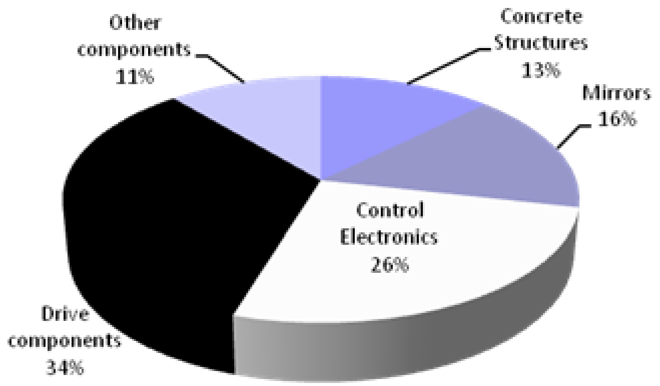
Preliminary design:

- Small (10-15 m^2) heliostat, factory-produced, PV self-powered, with wireless communication to minimize field wiring costs
- Factory-made, surface-installed concrete track foundation to simplify installation

Solar Hydrogen Production Preliminary System Comparison

	Area of Solar Reflectors [sq.km]	Land area [sq.km]	Total Capital Cost [$M]	**Cost of Hydrogen [$/kg]**
Baseline Hybrid Sulfur (HyS) System (Kolb): Heliostat/Central Receiver	1.30	6.50	381.2	**3.00**
Dish concentrator	0.85	3.42	409.2	**3.13**
FSEC S-NH_3 Cycle w/ Solar Boost:				
Dish concentrators w/cold mirror	0.83	3.33	644.3	**3.33**
Heliostat w/hot mirror	1.06	5.31	810.6	**4.12**
Heliostat-separate photoreactor	0.84	5.90	435.1	**2.33**
Advanced GRC Heliostat-separate rxr	0.84	5.90	417.4	**2.25**

- **Results:**
  - **FSEC process hydrogen cost <$3/kg**
  - Hot/cold mirror systems more expensive
  - FSEC process with separate photoreactor shows cost advantage over baseline (HyS)
  - Advanced heliostat improves costs further
- GRC prototype heliostat cost estimated at 17% less than conventional glass/metal heliostat **($105/sq.m vs. $126/sq.m)**



Future Work

- Close & complete analyses of S-NH_3 cycle
- Complete H_2 production photocatalyst screening
- Reduce noble metal loading on the photocatalyst
- Develop immobilized photocatalyst formulations
- Conclude oxygen production process optimization
- Analyze & design the high temperature reactor/receiver system
- Complete solar collector system analysis & design
- Perform technoeconomic & H2A analysis of the S-NH_3 cycle

Summary

- S-NH_3 photo/thermochemical water splitting cycle has been validated for solar hydrogen production
- S-NH_3 cycle utilizes the thermal portion of solar spectrum for the production of O_2 while the high energy photonic part of sunlight is used for hydrogen generation
- The 1st law efficiency of the S-NH3 cycle was calculated using Aspen flowsheeting & shown to be **51%**
- A large number of doped & polymer stabilized CdS based photocatalysts have been synthesized and evaluated for H_2 production from aqueous ammonium sulfite solutions
- Heliostat field appears to be the preferred solar concentrator approach
- GRC shows promise to lower heliostat field costs